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(54) 【発明の名称】 生分解性複合繊維

(57)【要約】

【目的】 製糸性良く製造することができ、生分解性及 び染色性の度合いの異なる繊維とすることが可能な生分 解性複合繊維を提供する。

【構成】 生分解性を有し、結晶化速度の異なる成分A 及び成分Bで構成された複合繊維であって、成分Aと成 分Bが機能断面において交互配列され、そのいずれもが 維維動方向に連載するとともに繊維表面に露出している 交互配列型の生分解性複合纖維。

【特許請求の範囲】

【請求項1】 生分解性を有し、結晶化速度の異なる成分A及び成分Bで構成された複合繳罐であって、成分Aと成分Bとが纖維断面において交互に配列され、そのいずれもが纖維軸方向に連続するとともに繊維表面に露出していることを特徴とする交互配列型の生分解性複合繳維。

【請求項2】 成分Aがモル比 100/0~90/10の範囲 のポリプチレンサクシネートとポリエチレンサクシネート、ポリプチレンアジペート又はポリプチレンセバケー 10 トとの共重合体であり、成分Bがモル比85/15~65/35 の範囲のポリプチレンサクシネートとポリエチレンサクシネート、ポリプチレンアジペート又はポリプチレンセバケートとの共重合体である請求項1記載の生分解性複合機能。

【請求項3】 成分Aと成分Bとの配列数合計が12以上であり、成分Aと成分Bとの複合重量比が1/1~3/1である請求項1又は2記載の生分解性複合繊維。

【発明の詳細な説明】

[0001]

【産業上の利用分野】本発明は、製糸性良く製造することができ、生分解性や染色性の度合いの異なる繊維とすることが可能な生分解性複合繊維に関するものである。 【0002】

【従来の技術】従来、溶融紡糸法によって生分解性繊維 を製造する場合、紡出されたフィラメントは冷却風吹き 付けによって冷却固化させ、その後延伸する方法が採用 されている。

【0003】しかし、生分解性に優れたポリマーは結晶 化温度が室温より低く、また、結晶化速度の遅いものが 30 多く、紡出糸条は、通常の冷却風吹き付けによる冷却だ けでは冷却不足のために固化できず、ブロッキングが生 じていた。

【0004】この問題の解決策として、冷却風温を下げたり、冷却時間を長くしたり、冷却風速を増大させたりすることが考えられる。しかし、冷却風温を下げる方法では、やはり十分な冷却ができず、冷却時間を長くするには装置的な制約があり、冷却風速を増大させる方法では、糸揺れが生じて逆にフィラメント同士が密着するという問題があった。

【0005】また、種々の生分解性ポリマーが提案されているが、用途に応じて生分解性や染色性の度合いの異なる繊維が要望さている。

[0006]

【発明が解決しようとする課題】本発明は、結晶化温度が低く、結晶化速度の遅い生分解性ポリマーからなり、製糸性良く製造することができ、生分解性や染色性の度合いの異なる繊維を得ることが可能な生分解性複合繊維を提供しようとするものである。

[0007]

【課題を解決するための手段】本発明は、上記の課題を解決するもので、その要旨は、生分解性を有し、結晶化速度の異なる成分A及び成分Bで構成された複合繊維であって、成分Aと成分Bとが繊維断面において交互に配列され、そのいずれもが繊維動方向に連続するとともに繊維表面に露出していることを特徴とする交互配列型の生分解性複合繊維にある。

【0008】以下、本発明について詳細に説明する。

【0009】成分Aとしては、モル比 100/0 ~90/10 の範囲のポリブチレンサクシネート (PBS) とポリエチレンサクシネート (PBS)、ポリブチレンアジペート (PBA) 又はポリブチレンセバケート (PBSe) との共重合体が好ましく用いられる。

【0010】また、成分Bとしては、モル比85/15~65/35、好ましく85/15~70/30の範囲のPBSとPES、PBA又はPBSeとの共重合体が好ましく用いられる。

【0011】A成分のPBSの割合が上記範囲より少ないと製糸性が劣り、成分BのPBSの割合が上記範囲より多いと生分解性及び染色性に劣り、少ないと耐熱性及び得られる繊維の糸質性能が劣ったものとなる。

【0012】これらのポリマーは、数平均分子量が 200 00以上、好ましくは 30000以上のものが製糸性及び得られる繊維の特性の点で望ましい。

【0013】紡糸に供するボリマーには、炭酸カルシウム、二酸化チタン、アルミナ、シリカ、タルク等の無機系結晶核剤を0.01~5重量%、好ましくは0.05~2重量%含有させることが望ましい。

【0014】溶融紡糸温度は、用いるポリマーの融点及 び分子量によって異なるが、150~280 でとすることが 望ましい。紡糸温度が 150℃未満では溶融押し出しが困 難であり、 280℃を超えるとポリマーの分解が顕著とな り、高強度の繊維を得ることが困難となる。

【0015】成分Aと成分Bは繊維断面において交互に配列され、そのいずれもが繊維軸方向に連続し、繊維表面に露出していることが必要である。生分解性ポリマーでは、一般に、結晶性の良いポリマーは分解速度が遅く、染色性が悪いという性質を有し、逆に、結晶性の低いポリマーは染色性及び生分解性に優れた性質を有している。成分Aのような結晶性の良いポリマーを単一型又は芯鞘型の鞘部に用いると、繊維表面の全てがそれで覆われるため、ブロッキングは防げるが、生分解性及び染色性に劣る。しかし、成分Bのような結晶性の低いポリマーを用いると、ブロッキングが生じて製糸性が悪くなる。そこで、両成分を繊維表面に露出させることにより、優れた製糸性と優れた生分解性及び染色性を有する繊維が得ることが可能となる。

【0016】成分Aと成分Bとの配列数の合計は12以上であることが好ましい。配列数が少なくなると、1列の 30 繊維表面に占める面積が大きくなり、十分な冷却性能、 生分解性能及び染色性能が得られなくなる。また、配列 数を変えることによりこれらの性能の異なる繊維とする ことが可能となる。

【0017】成分Aと成分Bとの複合重量比は1/1~3/1であることが好ましい。成分Aが上記の範囲より多くなると、生分解性及び染色性に劣り、少なくなるとブロッキングが生じやすく、製糸性が悪くなる。さらに、この複合比を変えることにより、これらの性能の異なる繊維とすることが可能となる。

【0018】溶融紡出された糸条は、紡糸口金直下に数 10 置された環状又は横型吹き付けにより冷却される。冷却 固化した糸条は、紡糸油剤を付与した後、300~3500m /分の速度で引きとられ、一旦巻き取った後又は巻き取ることなく連続して延伸される。紡糸油剤としては、通常のポリエステル繊維用紡糸油剤を使用することができる。

【0019】延伸は、室温、あるいは無ローラ等を用い、1段又は多段階で行われる。高強度の繊維を得るには、多段階で延伸することが望ましく、第2段目の延伸時に、無ローラと延伸ローラの間で熱プレート又は熱オ 20ーブンを使用してもよい。特に、寸法安定性が必要な場合、延伸に引き続き定長無処理又は弛緩無処理を加えることが望ましい。このようにして、実用に耐え得る一定の糸質性能、生分解性及び染色性を有する交互配列型複合繊維を製造することができる。

[0020]

【実施例】次に、本発明を実施例により具体的に説明する。なお、測定、評価法は次のとおりである。

引張強伸度

*JIS L 1013に準じて測定を行った。

生分解性

7月から10月にかけての3カ月間、試料を土壌中に埋設した後に取り出して強度を測定し、強度保持率が50%未満のものを○、50%以上のものを△として評価した。

4

染色性

Resolin Blue (バイエル社製分散染料) を 1 %owf 使用し、浴比 1 / 100 、70℃で15分間染色し、PBS 100%のものをコントロールとして比較し、良好なものを○、

0 あまり差がないものを△として評価した。

【0021】実施例1

成分Aとして数平均分子量が 40000のPBS、成分Bとしてモル比が80/20であるPBSとPESとの共重合体に 0.1重量%の二酸化チタンを添加したものを用い、エクストルーダー型溶融紡糸機に供給し、紡糸温度 170°Cで、繊維断面において成分Aと成分Bとが放射状に交互に配列された配列数12の繊維となる紡糸口金から溶融紡出し、模型吹き付けにより冷却固化させ、水系エマルジョン油剤を付与した後、 400m/分の速度で引き取り、連続して第一段目延伸倍率 1.5倍、第二段目延伸倍率 2.7倍、総延伸倍率的 4.1°で延伸を行い、 315d/36f

の交互配列型複合繊維を得た。 【0022】実施例2~4及び比較例1~8 表1に示す条件で、実施例1と同様に製糸を行った。実

施例1~4及び比較例1~8で得られた複合纖維の特性

値を表1に示す。 【0023】

【表1】

			*										
	共通合理技(そか比)		野歌		主度	仲 皮		杂色性					
	业分 A	政 会 B	·	8	9	00	# =						
1	798/798 =100/ 0	PBS/PBS = 80/20	12	1 /1	5.7	28.7	0	0					
2	196/TBA = 98/10	PBS/FBA = 70/30	16	VI	4.7	36,5	0	0					
3	PES/PES = 98/10	755/F84 = 80/20	16	2/1	5.1	30.8	0	0					
4	PBS/PBS = 982/10	PBS/PBS= 80/20	21	3/1	5.2	29.4	0	0					
1	PSS/PSS =108/ 0	-		1/0	6.1	28,1	Δ	2 10-1					
2	P85/FBA = 76/30	-	_	1/0	-	1	_	-					
3	PBS/PBS= 80/20	-	_	1/0	_	-	-	-					
4	PBS/PBS = 88/20	PBS/FBA = 70/30	16	2/1	-	-	: -	-					
5	PBS/FBA = 98/10	PBS/PBS== 80/40	36	3/1	-	-	-	-					
8	PBS/PBS= 98/10	PBS/PBS = 90/10	12	2/1	5.3	27.6	Δ	Δ					
7	PBS/PBS = 98/10	PBS/FBS = 80/20	8	3/1	-	-	_	-					
8	P65/P65 =108/ 0	FBS/FBS = 80/70	16	1/2	-	-	-	_					
	2 3 4 1 2 3 4 5 8 7	1 FBS/FBS = 101/0 2 FBS/FBS = 91/10 3 FBS/FBS = 91/10 4 FBS/FBS = 91/10 1 FBS/FBS = 101/0 2 FBS/FBS = 30/20 4 FBS/FBS = 91/10 5 FBS/FBS = 91/10 7 FBS/FBS = 91/10	1 FES/FES = 108/ 0 FES/FES = 80/ 20 2 FES/FES = 98/ 10 FES/FES = 70/ 30 3 FES/FES = 98/ 10 FES/FES = 80/ 20 4 FES/FES = 98/ 10 FES/FES = 80/ 20 1 FES/FES = 108/ 0 2 FES/FES = 70/ 30 3 FES/FES = 98/ 20 FES/FES = 70/ 30 5 FES/FES = 98/ 20 FES/FES = 80/ 30 6 FES/FES = 98/ 10 FES/FES = 90/ 10 7 FES/FES = 98/ 10 FES/FES = 80/ 20 8 FES/FES = 98/ 10 FES/FES = 80/ 20 8 FES/FES = 108/ 0 FES/FES = 80/ 20	1 FREATRS =101/0 FREATRS = 80/20 12 2 FREATRS = 91/10 FREATRS = 70/30 16 3 FREATRS = 91/10 FREATRS = 80/20 16 4 FREATRS = 91/10 FREATRS = 80/20 24 1 FREATRS = 101/0	1 FISAPIS = 101 0 FISAPIS = 80/20 12 3/1 2 FISAPIS = 91/10 FISAPIS = 70/30 16 1/1 3 FISAPIS = 91/10 FISAPIS = 80/20 10 2/1 4 FISAPIS = 91/10 FISAPIS = 80/20 24 3/1 1 FISAPIS = 101/0 1/0 2 FISAPIS = 70/30 1/0 3 FISAPIS = 80/20 FISAPIS = 70/30 16 2/1 4 FISAPIS = 80/20 FISAPIS = 70/30 16 2/1 5 FISAPIS = 91/10 FISAPIS = 80/40 36 3/1 6 FISAPIS = 91/10 FISAPIS = 90/10 12 2/1 7 FISAPIS = 91/10 FISAPIS = 80/20 8 3/1 8 FISAPIS = 101/0 FISAPIS = 80/20 8 3/1	## ## ## ## ## ## ## ## ## ## ## ## ##	#2	#2					

注:比較例2~5及び比較例7~8では、ブロッキングが発生した。

【0024】実施例1~4では、フィラメント間にブロ ※ブロッキングが生じ、比較例1及び6では、生分解性及ッキングもなく、良好な特性を有する複合繊維が得られ び染色性の劣ったものしか得られなかった。 たが、比較例2~5及び7~8では、フィラメント間に※50 【0025】 5

【発明の効果】本発明によれば、製糸性良く製造するこ することが可能な生分解性複合繊維が提供される。 とができ、生分解性及び染色性の度合いの異なる繊維と

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Title of the Invention: Biodegradable composite fibers

Abstract

Purpose:

To provide biodegradable composite fibers which can be can be manufactured with good thread forming properties and with which fibers which have different degrees of dyeability and biodegradability can be made. Constitution:

Biodegradable composite fibers of an alternating arrangement type which are composite fibers constructed with component A and component B which have biodegradability and different crystallization rates, in which component A and component B are exposed at the fiber surface, being arranged alternately in the fiber cross section and both continuing in the fiber axis direction.

Scope of the Patent Claims

· · [Claim 1]

Alternating arrangement type biodegradable composite fiber, characterized in that it is a composite fiber constructed with component A and component B which have biodegradability and of which the crystallization rates are different, and component A and component B are exposed at the fiber surface arranged alternately in the fibre cross section and both continuing in the fibre axis direction.

[Claim 2]

Biodegradable composite fiber, according to claim 1, wherein component λ is a copolymer of polybutylene succinate and polyethylene succinate, polybutylene adipate or polybutylene sebacate of molar ratio within the range from 100/0 to 9J/10, and component B is copolymer of polybutylene succinate and polyethylene succinate, polybutylene adipate or polybutylene sebacate of molar ratio within the range from 85/15 to 65/35.

[Claim 3]

Biodegradable composite fiber, according to claim 1 or claim 2, wherein the total number of sequences of component A and component B is at least 12, and the composite ratio by weight of component A and component B is from 1/1 to 3/1.

Detailed Description of the Invention
[0001]

Industrial Field of Application

The invention concerns biodegradable composite fibers which can be made with good thread forming properties and with which fibers which have different degrees of dyeability and biodegradability can be made.

[0002]

Prior Art

Methods in which the spun filaments are cooled and solidified by blowing with a cold draught and then drawn have been adopted in the past for the manufacture of biodegradable fibers by the melt spinning method.

[0003]

However, polymers which have excellent biodegradability have crystallization temperatures below room temperature and, moreover, many have a low crystallization rate and it is impossible to achieve solidification by cooling by blowing with cold draught in the usual way among the spinning conditions, and so inadequate cooling and blocking have occurred.

[0004]

The cooling draught temperature

The cooling draught temperature has sometimes been lowered as a means of resolving this problem, the cooling time has sometimes been increased, and consideration has also been given to increasing the cooling draught velocity. However, it is still impossible to achieve adequate cooling with the methods in which the cooling

draught temperature is lowered, and limitations are imposed by the apparatus if the cooling time is increased, and with the methods where the cooling draught velocity is increased the fibers are caused to vibrate and there is a problem in that adjacent fibers stick together.

[0005]

Furthermore, various biodegradable fibers have been proposed, but fibers which have different degrees of dyeability and biodegradability corresponding to the application are required.

[0006]

Problems to be Resolved by the Invention

The present invention is intended to provide biodegradable composite fibers comprising biodegradable polymers of which the crystallization temperatures are low and which have different crystallization rate, which can be produced with good thread forming properties, and with which fibers which have different degrees of dyeability and biodegradability can be obtained.

[0007]

Means of Resolving these Problems

The present invention is intended to resolve the abovementioned problems, being in outline an alternating arrangement type biodegradable composite fiber, characterized in that it is a composite fiber constructed with component A and component B which have biodegradability and of which the crystallization rates

are different, and component A and component B are exposed at the fiber surface arranged alternately in the fibre cross section and both continuing in the fibre axis direction.

[8000]

The invention is described in detail below.
[0009]

A copolymer of polybutylene succinate (PBS) and polyethylene succinate (PES), polybutylene adipate (PBA) or polybutylene sebacate (PBSe) of molar ratio within the range from 100/0 to 90/10 is preferably used for component A.

[0010]

PBSe of molar ratio within the range from 85/15 to 65/35, and preferably within the range from 85/15 to 70/30, is preferably used for component B.

[0011]

If the proportion of PBS in component A is below the abovementioned range then the thread forming properties are poor, and if the proportion of PBS in the component B is above the aforementioned range then the biodegradability and dyeability are poor while if it is below this range then the heat resistance and the thread performance of the fiber obtained are poor.

[0012]

These polymers are preferably of number average molecular weight at least 20,000, and preferably at least

30,000, in view of the thread forming properties and the properties of the fibers which are obtained.

[0013]

Inorganic crystallization nucleating agents, such as calcium carbonate, titanium dioxide, alumina, silica and talc for example, are preferably included in the polymers supplied for spinning in amounts of from 0.01 to 5 wt%, and preferably in amounts of from 0.05 to 2 wt%. [0014]

The melt spinning temperature according to the melting points and molecular vergnts of the polymers which are being used, but it is preferably from 150 to 280°C. Melt extrusion is difficult at spinning temperature below 150°C, and above 280°C there is pronounced degradation of the polymers and it is difficult to obtain high strength fibers.

[0015]

alternately in the fiber cross section, both continue in the fiber axis direction, and be exposed at the fiber surface. With the biodegradable polymers, the polymers which have good crystallinity generally have a slow degradation rate and poor dyeability, while conversely the polymers which have a low crystallinity have excellent dyeability and biodegradability. When a polymer which has good crystallinity such as component A is used as a single type or as the sheath of a coresheath type, all of the fiber surface is covered with

this material and so blocking is impeded, but the biodegradability and dyeability are poor. However, when a polymer which has low crystallinity such as component B is used, blocking occurs and the thread forming properties are poor. Thus, by exposing both components at the fiber surface it is possible to obtain fibers which have excellent film forming properties and excellent biodegradability and dyeability.

[0016]

The total number of sequences of component A and component B is preferably at least 12. If the number of sequences is small then the area of the fiber surface occupied by one sequence is considerable and adequate cooling performance, biodegradable performance and dyeability performance are not obtained. Furthermore, it is possible to make fibers in which these characteristics are different by varying the number of sequences.

[0017]

The composite ratio by weight of component A and component B is preferably from 1/1 to 3/1. If the amount of component A exceeds the aforementioned range then the biodegradability and dyeability are poor, and if it is low then blocking is liable to occur and the thread making properties are poor. Moreover, it is possible to make fibers which differ in respect of performance by changing the composite ratio.

[0018]

The melt spun threads are cooled by means of

ring-like or transverse blower which is established immediately following the spinning die. The cooled and solidified threads are pulled at a rate of from 300 to 3500 m/minute after the application of a spinning oil agent and drawn after winding up or without being wound up. The usual polyester fiber type spinning oil agents can be used for the spinning oil agent.

[0019]

using a hot roller, for example, in one step or in a number of steps. The drawing is preferably carried out in a number of steps to obtain high strength fibers, and the hot roller can be used at the time of the second stage drawing with a hot plate or a hot oven between the drawing rolls. In cases where dimensional stability is required in particular, the addition of a continuous fixed length heat treatment or relaxation heat treatment to the drawing process is desirable. It is possible to manufacture alternating arrangement type composite fibers which have fixed thread performance, biodegradability and dyeability which are durable in practice in this way.

[0020]

Illustrative Examples

The invention is described below in practical terms by means of illustrative examples. Moreover, the methods used for measurement and evaluation purposes are described below.

Tensile Strength and Elasticity

These were measured in accordance with JIS L 1013.

Biodegradability

The samples were buried in the ground for 3 months from July to October and then recovered and the strength was measured, and those where the fractional retention of strength was less than 50% were evaluated as being of class 0 and those where it was 50% or above were evaluated as being of class A.

Dyeability

Samples were dyed for 15 minutes at 70°C at a bath ratio of 1/100 using 1 % owf of Resolin Blue (a disperse dye manufactured by the Bayer Co.) and compared with a 100% PBS sample as a control, and those which were good were evaluated as class 0 and those where there was no real difference were evaluated as class A.

[0021] Example 1

Melt spinning was carried out using PBS of number average molecular weight 40,000 for component A and material obtained by adding 0.1 wt% of titanium dioxide to a copolymer of PBS and PES of molar ratio 80/20 for component B, supplying the materials to an extruder type melt spinning machine so as to produce from the spinning die threads with an arrangement number of 12 where component A and component B were radially arranged alternately in the fiber cross section at a spinning temperature of 170°C, and the threads were then cooled and solidified by transverse blowing and, after applying

a water base oiling agent emulsion, they were pulled at a rate of 400 m/minute and then subjected to first stage drawing at a drawing factor of 1.5 times and second stage drawing at a drawing factor of 2.7 times, the drawing being carried out to an overall drawing factor of about 4.1, and alternating arrangement type composite fibers of 315 d/36f were obtained.

[0022] Examples 2 to 4 and Comparative Examples 1 to 8

Threads were made in the same way as in Example 1 but under the conditions shown in Table 1. The properties of the composite fibers obtained in Examples 1 to 4 and Comparative Examples 1 to 8 are shown in Table 1.

[0023]

Table 1

REY 1: Examples, 2: Comparative Examples, 3: Copolymer Composition (molar ratio), 4: Component A, 5: Component B, 6: Arrangement Number, 7: Composition Ratio by Weight, A/B, 8: Strength (g/d), 9: Elasticity (%), 10: Biodegradability, 11: Dyeability, 12: Control, 13: NOTE: Blocking occurred in Comparative Examples 2 to 5 and Comparative Examples 7 and 8.

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		12.9 A	建分号		М	40	60		
	1	PM/PM -100/ 0	78/78 - 10/30	12	N	5.7	21	0	0
	2	766/FEA = 91/10	76/76 = 70/30	15	И	47	35.5	0	0
	3	TS/TS - SI/10	75/75 - 80/2D	ie.	2/1	51	32.8	0	0
7	4	FE/FE - 91/10	MA/ROW 82/20	×	И	5.2	24	0	0
	1	76/15 =101/ 0	_		N	61	21	Δ	210-1
Ħ	2	16/15A - 16/20	-	-	1/0	-	-	-	-
	3	PE/TEN- 50/20	-	-	N	-	-	-	-
	4	76/76 · SI/30	REAL - NAT	15	2/1	-		-	
	5	PEL/TEL = 91/10	MS/MS- 82/ 63	*	N	-	-	-	-
,	6	PE/TE- 91/30	FEC/763 = 90/10	12	n	5.3	21.8	Δ	Δ
	7	FE/FE - 91/30	PE/RE - 50/20	1	ท	-	-	-	-
	8	PE/FES =101/ 0	75/75 - E/20	15	VZ	Γ-	-	-	-

[0024]

在:比較何2~5及び比較例7~8では、ブロッキングが発生した。

There was no blocking between filaments and composite fibers which had good properties were obtained in Examples 1 to 4, but blocking between filaments occurred in Comparative Examples 2 to 5 and Comparative Examples 7 and 8, and only fibers which had poor biodegradability and dyeability were obtained in Comparative Examples 1 and 6.

[0025]

Effect of the Invention

By means of this invention there are provided biodegradable composite fibers which can be produced with good fiber forming properties and which can be fibers which have different degrees of biodegradability and dyeability.